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(54) Title: POSITIVE-WORKING INFRARED RADIATION SENSITIVE COMPOSITION AND PRINTING PLATE AND IMAGING METHOD (57) Abstract A positive-working lithographic printing plate is used to provide a positive image without a post-exposure baking step and without any floodwise exposure steps. The printing plate includes a layer that is imageable using an infrared radiation laser. This layer consists essentially of a phenolic resin, an infrared radiation absorbing compound, and a dissolution inhibitor that is non-photosensitive and is capable of providing sites for hydrogen bonding with the phenolic moieties of the binder resin.		

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POSITIVE-WORKING INFRARED RADIATION SENSITIVE
COMPOSITION AND PRINTING PLATE AND IMAGING METHOD

5 This invention relates to a positive-working
imaging composition and printing plate that is
sensitive to infrared radiation. It also relates to a
method of forming a positive image using such printing
plates.

10 The art of lithographic printing is based
upon the immiscibility of oil and water, wherein the
oily material or ink is preferentially retained by the
image areas and the water or fountain solution is
preferentially retained by the nonimage areas. When a
15 suitably prepared surface is moistened with water and
an ink is then applied, the background or nonimage
areas retain the water and repel the ink while the
image areas accept the ink and repel the water. The
ink on the image areas is then transferred to the
surface of a material upon which the image is to be
20 reproduced, such as paper, cloth and other materials.
Commonly, the ink is transferred to an intermediate
material called the blanket which in turn transfers the
ink to the surface of the material upon which the image
is to be reproduced.

25 A widely used type of lithographic printing
plate has a light-sensitive coating applied to an
aluminum base support. The coating may respond to
light by having the portion that is exposed become
hardened so that nonimage areas are removed in the
30 developing process. Such a plate is referred to in the
art as a negative-working printing plate. Conversely,
when those portions of the coating that are exposed
become soluble so that they are removed during
development, the plate is referred to as a positive-

working plate. In both instances, the coating remaining on the plate is ink-receptive or oleophilic and the nonimage areas or background are water-receptive or hydrophilic. The differentiation between image and nonimage areas is made in the exposure process where a film is applied to the plate with a vacuum to insure good contact. The plate is then exposed to a light source, a portion of which is composed of UV radiation. In the instance of positive-working plates, the areas on the film corresponding to the image areas are darkened, preventing light from making those plate coating areas developer soluble, while the areas on the film corresponding to the plate nonimage areas are clear, allowing them to become soluble. The solubilized plate image areas can be removed during development. The nonimage areas of a positive-working plate remain after development, are oleophilic and will accept ink while the exposed areas that have had the coating removed through the action of a developer are desensitized and are therefore hydrophilic.

Various useful printing plates that can be either negative-working or positive-working are described, for example, in GB 2,082,339 and US-A-4,927,741, both of which describe imaging layers containing an o-diazoquinone and a resole resin, and optionally a novolac resin. Another plate that can be similarly used is described in US-A-4,708,925 wherein the imaging layer comprises a phenolic resin and a radiation-sensitive onium salt. This imaging composition can also be used for the preparation of a direct laser addressable printing plate, that is imaging without the use of a photographic transparency.

Printing plates comprising imaging layers that contain novolac resins, infrared radiation absorbing compounds and other materials are described, for example, in US-A-5,340,699, US-A-5,372,907, US-A-5,372,917, US-A-5,466,557 and EP-A-0 672 954. Imaging with these plates includes exposure to near-infrared energy to produce acids in an imagewise fashion. These acids catalyze crosslinking of the coating in a post-exposure heating step. Precise temperature control is required in the heating step.

DE-4,426,820 describes a printing plate that can be imaged in the near infrared at moderate power levels with relatively simple processing requirements. This printing plate has at least two layers: an imaging layer containing an o-diazoquinone compound and an infrared radiation absorbing compound, and a protective overcoat containing a water-soluble polymer or silicone polymer. This plate is floodwise exposed with ultraviolet light to convert the o-diazoquinone to an indenecarboxylic acid, which is then imagewise decarboxylated by means of heat transferred from the infrared radiation absorbing material. Development with an alkaline solution results in removal of areas not subjected to thermal decarboxylation. The pre-imaging floodwise exposure step, however, is awkward in that it precludes the direct loading of the printing plates into plate-setters.

Optical recording media having laser imageable layers are described in US-A-4,966,798. Such layers contain an infrared radiation absorbing dye or pigment in a phenolic resin, and are resident on a suitable polymeric support. Recordation is carried out using a laser to bring about a surface change in the

imageable layer. Printing plates are different materials and require a different imaging process.

However, there is a need to increase the processing latitude of these printing plates so that
5 the development conditions need not be so carefully controlled in order to provide desired discrimination between image and nonimage areas. Processing latitude can be increased by incorporating diazonaphthoquinones, but in order to preserve the positive-working nature of
10 such materials, the amount of the IR absorbing compounds must be restricted below certain threshold levels. The presence of diazonaphthoquinones also makes such printing plates more sensitive to room light, negating one advantage of so-called "thermal" printing
15 plates.

Thus, there is a need for simple printing plates that can be easily imaged in the near infrared at moderate power levels and that require relatively simple processing methods. It is also desired that
20 such printing plates have improved processing latitude without the disadvantages presented by the use of diazonaphthoquinones.

The present invention provides a positive-working imaging composition consisting essentially of a
25 phenolic binder resin, and an infrared radiation absorbing compound,

the composition characterized as further including a non-photosensitive compound capable of providing sites for hydrogen bonding with the phenolic
30 moieties of the binder resin.

This invention also provides a positive-working lithographic printing plate comprising a support and characterized as having thereon an imaging

layer formed from the imaging composition described above.

Still further, a method for providing a positive image consists essentially of the steps of:

- 5 A) imagewise exposing the positive-working lithographic printing plate described above with an infrared radiation emitting laser, and
- B) contacting the element with an aqueous developing solution to remove the image areas of the
- 10 positive-working printing plate.

The printing plates of this invention are useful for providing high quality positive images using moderately powered lasers. Since the printing plates are infrared radiation sensitive, digital imaging

15 information can be conveniently utilized to form continuous or halftone positive images. The printing plate is simple in construction, having only a single imaging layer that consists essentially of only three components: a phenolic binder resin, an IR absorbing

20 compound, and a compound that is considered a "dissolution inhibitor". Such a compound inhibits the dissolution of the phenolic binder resin by providing hydrogen acceptor sites for hydrogen bonding with the phenolic moieties of the binder resin. This allows one

25 to formulate the composition to optimize the amount of IR absorbing compound independently of its effect on the rate of resin dissolution.

After laser imaging, conventional development is the only other step needed to provide a positive

30 image. No pre-imaging or post-imaging flood exposure, or post-imaging baking, step is necessary in the practice of this invention. There is greater flexibility in the selection of developer solutions and development times and temperatures. Moreover, the

compounds used as dissolution inhibitors are non-photosensitive so the plates can be readily handled in room light.

The phenolic binder resins useful in the practice of this invention include any alkali soluble resin having a reactive hydroxy group. The phenolic binder resins are light-stable, water-insoluble, alkali-soluble film-forming resins that have a multiplicity of hydroxy groups either on the backbone of the resin or on pendant groups. The resins typically have a molecular weight of at least 350, and preferably of at least 1000, as determined by gel permeation chromatography. An upper limit of the molecular weight would be readily apparent to one skilled in the art, but practically it is 100,000. The resins also generally have a pKa of not more than 11 and as low as 7.

As used herein, the term "phenolic resin" also includes what are known as novolac resins, resole resins and polyvinyl compounds having phenolic hydroxy groups. Novolac resins are preferred.

Novolac resins are generally polymers that are produced by the condensation reaction of phenols and an aldehyde, such as formaldehyde, or aldehyde-releasing compound capable of undergoing phenol-aldehyde condensation, in the presence of an acid catalyst. Typical novolac resins include phenol-formaldehyde resin, cresol-formaldehyde resin, phenol-cresol-formaldehyde resin, p-t-butylphenol-formaldehyde resin, and pyrogallol-acetone resins. Such compounds are well known and described for example in US-A-4,308,368, US-A-4,845,008, US-A-5,437,952, US-A-5,491,046, US-A-5,143,816 and GB 1,546,633. A particularly useful novolac resin is

prepared by reacting *m*-cresol or phenol with formaldehyde using conventional conditions.

Phenolic resins that are known as "resole resins", including, for example, condensation
5 products of bis-phenol A and formaldehyde, are also useful in this invention.

Still another useful phenolic binder resin is a polyvinyl compound having phenolic hydroxyl groups. Such compounds include polyhydroxystyrenes
10 and copolymers containing recurring units of a hydroxystyrene, and polymers and copolymers containing recurring units of halogenated hydroxystyrenes. Such polymers are described for example in US-A-4,845,008.

15 Other useful novolacs are described in US-A-4,306,010 and US-A-4,306,011. Still other useful phenolic resins are described in US-A-5,368,977.

A mixture of the resins described above can be used, but preferably, a single novolac resin is
20 present as the binder resin in the imaging composition of this invention.

When the imaging composition of this invention is formulated as a coating composition in suitable coating solvents, the binder resin is
25 present in an amount of at least 0.5 weight percent (wet composition). Preferably, it is present in an amount of from 1 to 10 weight percent.

In the dried imaging layer of the printing plate, the binder resin is the predominant material.
30 Generally, it comprises at least 50 weight percent, and more preferably from 60 to 88 weight percent, of the dried layer.

The second essential component of the imaging composition of this invention is an IR

absorbing compound, or a mixture thereof. Such compounds typically have a maximum absorption wavelength (λ_{max}) in the region of at least 700 nm, that is in the infrared and near infrared regions of the spectrum, and more particularly, within from 800 to 1100 nm. Particularly useful IR dyes are those having high extinction coefficients at wavelengths corresponding to the output of commercially available lasers (such as at 784 nm, 830 nm, 873 nm and 981 nm), Nd:YLF lasers (1053 nm) and ND:YAG lasers (1064 nm). Carbon black and other pigments, or dyes having broad spectral absorption characteristics are also useful as IR absorbing compounds. Mixtures of dyes, pigments, or dyes and pigments can also be used so that a given composition can be imaged at multiple wave lengths.

Classes of materials that are useful include squarylium, croconate, cyanine (including phthalocyanine), merocyanine, chalcogenopyrroloarylidene, oxyindolizine, quinoid, indolizine, pyrylium and metal dithiolene dyes or pigments. Other useful classes include thiazine, azulenium and xanthene dyes. Particularly useful IR absorbing dyes are of the cyanine class. Other useful cyanine IR absorbing dyes are described in US-A-4,973,572.

The amount of IR absorbing compound in the dried imaging layer is generally sufficient to provide an optical density of at least 0.05 in the layer, and preferably, an optical density of from 0.5 to 2. This range would accommodate a wide variety of compounds having vastly different extinction coefficients. Generally, this is at least 0.1 weight

percent, and preferably from 1 to 20 weight percent of the dry coating weight.

The weight ratio of the IR absorbing compound to phenolic binder resin is at least 1:1000, and preferably from 1:200 to 1:10. The optimum ratio will depend upon the phenolic binder resin and IR absorbing compound being used, and can be determined with routine experimentation.

One or more "dissolution inhibitor compounds" are present in the imaging composition of this invention as the third essential component. Such compounds have polar functionality that serve as acceptor sites for hydrogen bonding with hydroxy groups on aromatic rings. The acceptor sites are atoms with high electron density, preferably selected from electronegative first row elements. Useful polar groups include keto groups (including vinylogous esters). Other groups may also be useful, such as sulfones, sulfoxides, thiones, phosphine oxides, nitriles, imides, amides, thiols, ethers, alcohols, ureas as well as nitroso, azo, azoxy, nitro and halo groups. In general, it is desired that such compounds have an "inhibition factor" of at least 0.5, and preferably at least 5 and more preferably, at least 15. The higher this value is, the more useful is the compound in this invention.

Inhibition factors for given compounds can be readily measured using the procedure described by Shih and others, *Macromolecules*, Vol. 27, p. 3330 (1994). The inhibition factor is the slope of the line obtained by plotting the log of the development rate as a function of inhibitor concentration in the phenolic resin coating. Development rates are conveniently measured by laser interferometry, as

described by Meyerhofer in *IEEE Trans. Electron Devices*, ED-27, 921 (1980).

Representative compounds having the desired properties reported dissolution (inhibition factors listed in parentheses) include aromatic ketones including xanthenes (2.26), flavanones (6.80), flavones (18.3), 2,3-diphenyl-1-indenones (23.6), pyrones (including thiopyrones), and 1'-(2'-acetoneaphthonyl)benzoate, and include such compounds as α - and β -naphthoflavone (49.1 and 46.6, respectively), 2,6-diphenyl-4H-pyran-4-one, 2,6-diphenylpyrone, 2,6-diphenylthiopyrone, 2,6-di-*t*-butylthiopyrone and 2,6-diphenyl-4H-thiopyran-4-one. The flavones and pyrones preferred are α -naphthoflavone, 2,6-diphenyl-4H-pyran-4-one and 2,6-diphenyl-4H-thiopyran-4-one.

The dissolution inhibitors useful in the present invention are not themselves actually sensitive to near-IR radiation. Their dissolution inhibition abilities are presumably altered by the localized heating that results from irradiation of the IR absorbing compound. Thus, by "non-photosensitive" is meant that these compounds are not significantly sensitive to actinic radiation having a wavelength above 400 nm, and preferably above 300 nm. Thus, the conventional photosensitive *o*-naphthoquinonediazides are not useful in this invention.

The weight ratio of the dissolution inhibitor compound to phenolic binder resin is at least 1:100, and preferably from 5:100 to 40:100. The optimum weight ratio will depend upon the inhibition factor of the dissolution inhibitor

compound, the phenolic resin binder, the amount and type of IR radiation absorbing compound, the amount and type of other addenda, and the developer composition used, and can be readily determined by routine experimentation by a skilled artisan. In the dry coating, the amount of dissolution inhibitor compound is generally at least 1% (based on total dry weight).

Optional, non-essential components of the imaging composition of this invention include colorants, development accelerators, cross-linking agents, sensitizers, stabilizers, exposure indicators and surfactants in conventional amounts.

Obviously, the imaging composition is coated out of one or more suitable organic solvents that have no effect on the sensitivity of the composition, and in which all components are soluble or dispersible. Various solvents for this purpose are well known, but acetone and 1-methoxy-2-propanol are preferred. Mixtures can be used if desired. The essential components of the composition are dissolved in the solvents in suitable proportions to provide the desired dry amounts.

Suitable conditions for drying the imaging composition involve heating for a period of time of from 0.5 to 5 minutes at a temperature in the range of from 20 to 300 °C.

To form a printing plate of this invention, the imaging composition is applied (usually by coating techniques) onto a suitable support, such as a metal sheet, polymeric film (such as a polyester), ceramics or polymeric-coated paper using conventional procedures and equipment. Suitable metals include aluminum, zinc or steel, but preferably, the metal is

aluminum. A most preferred support is an electrochemically grained and sulfuric acid anodized aluminum sheet, that can be further treated with an acrylamide-vinylphosphonic acid copolymer according to the teaching in US-A-5,368,974.

The thickness of the resulting positive-working imaging layer, after drying, on the support can vary widely, but typically it is in the range of from 0.5 to 2 μm , and preferably from 1 to 1.5 μm .

No other essential layers are provided on the printing plate. In particular, there are no protective or other type of layers over the imaging layer. Optional, but not preferred subbing or antihalation layers can be disposed under the imaging layer, or on the backside of the support (such as when the support is a transparent polymeric film).

The printing plates are uniquely adapted for "direct-to-plate" imaging applications. Such systems utilize digitized image information, as stored on a computer disk, compact disk, computer tape or other digital information storage media, or information that can be provided directly from a scanner, that is intended to be printed. The bits of information in a digitized record correspond to the image elements or pixels of the image to be printed. This pixel record is used to control the exposure device, that is a modulated laser beam. The position of the laser beam can be controlled using any suitable means known in the art, and turned on and off in correspondence with pixels to be printed. The exposing beam is focused onto the unexposed printing plate. Thus, no exposed and processed films are needed for imaging of the plate, as in the conventional lithographic imaging processes.

Laser imaging can be carried out using any moderate or high-intensity laser writing device. Specifically, a laser printing apparatus is provided that includes a mechanism for scanning the write beam across the element to generate an image without ablation. The intensity of the write beam generated at the laser diode source at the printing plate is at least $0.2 \text{ mW}/\mu^2$. During operation, the plate to be exposed is placed in the retaining mechanism of the writing device and the write beam is scanned across the plate to generate an image.

Following laser imaging, the printing plate of this invention is then developed in an alkaline developer solution until the image areas are removed to provide the desired positive image. Development can be carried out under conventional conditions for from 30 to 120 seconds. One useful aqueous alkaline developer solution is a silicate solution containing an alkali metal silicate or metasilicate. Such a developer solution can be obtained from Eastman Kodak Company as KODAK Production Series Machine Developer/Positive.

After development, the element can be treated with a finisher such as gum arabic, if desired. However, no other essential steps besides development is needed. Thus, no post-imaging bake step is carried out, nor is floodwise exposure needed before or after imaging.

The following examples are provided to illustrate the practice of this invention, and not to limit it in any manner. Unless otherwise noted, all percentages are by weight.

Examples 1-3:

Four imaging coating formulations were prepared as shown in the following TABLE I:

5

TABLE I

<u>COMPONENT</u>	<u>PARTS BY WEIGHT</u>			
	Example 1	Example 2	Example 3	Control A
Cresol-formaldehyde novolak resin	5.206	5.206	5.206	5.206
CG-21-1005 dye (Ciba Geigy)	0.108	0.108	0.108	0.108
2-[2-[2-Chloro-3-[(1,3-dihydro-1,1,3-trimethyl-2H-benz[e]indol-2-ylidene)ethylidene-1-cyclohexen-1-yl]-ethenyl]-1,1,3-trimethyl-1H-benz[e]indolium, salt with 4-methylbenzenesulfonic acid as IR dye	0.065	0.065	0.065	0.065
1'-(2'-Acetonaphthonyl)benzoate dissolution inhibitor	0.924	0	0	0
2,3-Diphenyl-1-indenone dissolution inhibitor	0	0.898	0	0
α -Naphthoflavone dissolution inhibitor	0	0	0.868	0
BYK-307*	0.011	0.011	0.011	0.011
Acetone	6.626	6.626	6.626	6.626
1-Methoxy-2-propanol	87.060	87.086	87.116	87.984

*BYK-307 is a polyether-modified polydimethylsiloxane available from BYK-Chemie.

10

In Examples 1-3, the dissolution inhibitors were used in equimolar proportions, but no dissolution inhibitor was included in the Control A formulation.

15

Each formulation was applied to give a dry coating weight of about 1.5 g/m² onto

electrochemically grained and sulfuric acid anodized aluminum supports that had been further treated with an acrylamide-vinylphosphonic acid copolymer (according to US-A-5,368,974, noted above) to form an
5 imaging layer in an unexposed lithographic printing plate.

A specific region or area of each plate was imaged on a commercially available EKTRON platesetter at 300 rpm and 250 milliwatts with a laser emitting a
10 modulated pulse centered at 830 nm. A region or area of each plate was left unexposed (nonimaged). The plates were then processed with KODAK Production Series Machine Developer/Positive for various time intervals to provide positive images. The optical
15 density of each plate was then measured in both the imaged and nonimaged areas. The "percent remaining coating" was estimated as follows:

$$\% \text{ Coating Remaining} = 100 \times \frac{(\text{Processed density} - \text{Background})}{(\text{Original density} - \text{Background})}$$

20

wherein "Background" refers to the density of the uncoated plate support. The results are shown in TABLE II below. These results indicate that in the absence of a dissolution inhibitor, the imaging layer
25 of the Control A plate was completely stripped from the support by the developer solution even with short development times.

All of the plates of the present invention, however, exhibited acceptable results, that is,
30 significant differences in the amount of imaging layer remaining in the nonimaged areas in comparison with the imaged areas.

TABLE II

Development Time		% Coating Remaining											
		5 seconds		10 seconds		20 seconds		40 seconds		80 seconds			
Plate		Exposed	Unexposed	Exposed	Unexposed	Exposed	Unexposed	Exposed	Unexposed	Exposed	Unexposed	Exposed	Unexposed
Example 1		62%	94%	29%	87%	3%	73%	0%	34%	0%	0%	0%	0%
Example 2		74%	96%	56%	93%	22%	85%	2%	67%	0%	20%	0%	20%
Example 3		73	99%	35%	99%	12%	97%	3%	92%	0%	74%	0%	74%
Control A		0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%

Examples 4-6:

The formulations shown in TABLE III below were used to prepare printing plates of the present invention:

TABLE III

<u>COMPONENT</u>	<u>PARTS BY WEIGHT</u>		
	<u>Example 4</u>	<u>Example 5</u>	<u>Example 6</u>
Cresol-formaldehyde novolak resin	4.940	4.940	4.940
CG-21-1005 dye (Ciba Geigy)	0.100	0.100	0.100
2-[2-[2-Chloro-3-[(1,3-dihydro-1,1,3-trimethyl-2H-benz[e]indol-2-ylidene)ethylidene-1-cyclohexen-1-yl]-ethenyl]-1,1,3-trimethyl-1H-benz[e]indolium, salt with 4-methylbenzene-sulfonic acid as IR dye	0.065	0	0
CYASORB** 165	0	0.434	0
Carbon black (8%) dispersion in toluene	0	0	5.383
α -Naphthoflavone dissolution inhibitor	1.085	0.868	0.651
BYK-307	0.011	0.011	0.011
Acetone	6.288	6.288	6.288
1-Methoxy-2-propanol	87.511	87.359	82.627

** CYASORB 165 is a dye commercially available from American Cyanamid.

10

Each of the printing plates was laser imaged (100 rpm/250 m Watts) and developed as described in Examples 1-3, to provide high resolution positive images. All three showed essentially no coating loss in the nonimaged areas of the imaging layers.

15

Printing plates were also prepared from the formulations of Examples 5 and 6, and imaged at 1064

nm on a commercially available Gerber 42/T
 platesetter, and similarly processed to provide high
 resolution positive images. The development
 conditions were not quite sufficient to completely
 5 clear the background (nonimaged areas) for the
 Example 5 plate.

Comparison Examples:

The formulations shown in TABLE IV below
 10 were similarly used to prepare printing plates that
 are outside this invention because of a
 photosensitive dissolution inhibitor used:

TABLE IV

15

<u>COMPONENT</u>	<u>PARTS BY WEIGHT</u>	
	Control B	Control C
Cresol-formaldehyde novolak resin	5.206	5.206
CG-21-1005 dye (Ciba Geigy)	0.108	0.108
2-[2-[2-Chloro-3-[(1,3-dihydro-1,1,3-trimethyl-2H-benz[e]indol-2-ylidene)ethylidene-1-cyclohexen-1-yl]-ethenyl]-1,1,3-tri-methyl-1H-benz[e]in-dolium, salt with 4-methylbenzene-sulfonic acid as IR dye	0.065	0.065
2,4-Bis(1,2-naphthoquinone-2-diazido-5-sulfonyloxy)benzophenone dissolution inhibitor	2.009	0.868
BYK-307	0.011	0.011
Acetone	6.626	6.626
1-Methoxy-2-propanol	85.975	87.116

The printing plates were imaged and
 processed as described in Examples 1-3 above. The
 imaged and nonimaged normalized thicknesses were

calculated as in those examples, and the results of percent coating remaining for different development times are summarized in the following TABLE V. The dissolution inhibitor used in the Control B plate was a photosensitive compound based on diazonaphthoquinone chemistry, and was present at the same molar concentration as the dissolution inhibitor of Example 1. The nonimaged area thickness loss was very low, as desired, but the exposed areas were not completely cleared even at the longest development time. The amount of dissolution inhibitor was decreased for Control C, providing improved development cleanout, but the nonimaged areas coating loss was unacceptable.

TABLE V

Coating	5 seconds		10 seconds		20 seconds		40 seconds		80 seconds	
	Exposed	Unexposed	Exposed	Unexposed	Exposed	Unexposed	Exposed	Unexposed	Exposed	Unexposed
Control B	83%	99%	74%	98%	62%	99%	34%	97%	7%	90%
Control C	14%	87%	1%	70%	0%	30%	0%	0%	0%	0%

Example 7:

Example 3 was repeated, but substituting 2,6-diphenylpyrone for the naphthoflavone as the dissolution inhibitor compound. TABLE VI below shows that excellent differences in dissolution rates were obtained between the imaged and non-imaged areas.

Example 8:

Example 3 was repeated, but substituting 2,6-diphenylthiopyrone for the naphthoflavone as the dissolution inhibitor compound. TABLE VI below shows that excellent differences in dissolution rates were obtained between the imaged and non-imaged areas.

Example 9:

Example 3 was repeated, but substituting 2,6-di-*t*-butylthiopyrone for the naphthoflavone as the dissolution inhibitor compound. TABLE VI below shows that acceptable differences in dissolution rates were obtained between the imaged and non-imaged areas.

TABLE VI

% Coating Remaining vs. development time for Examples 7-9

Development Time	5 seconds		10 seconds		20 seconds		40 seconds		80 seconds	
	Exposed	Unexposed	Exposed	Unexposed	Exposed	Unexposed	Exposed	Unexposed	Exposed	Unexposed
Plate										
Example 7	88%	99%	80%	100%	65%	96%	36%	96%	7%	90%
Example 8	-	-	81%	96%	74%	96%	55%	100%	17%	98%
Example 9	84%	100%	73%	95%	51%	93%	19%	84%	4%	69%

CLAIMS:

1. A positive-working imaging composition consisting essentially of a phenolic resin, and an infrared radiation absorbing compound,
5 the composition characterized as further including a non-photosensitive compound capable of providing sites for hydrogen bonding with the phenolic moieties of the binder resin.
- 10 2. The composition as claimed in claim 1 wherein the phenolic resin is a novolac resin.
- 15 3. The composition as claimed in either claim 1 or 2 wherein the infrared radiation absorbing compound is carbon black, or a squarylium, croconate, cyanine, merocyanine, indolizine, pyrylium or metal dithiolene dye or pigment that absorbs infrared radiation at a wavelength of from 800 to 1100 nm.
- 20 4. The composition as claimed in any of claims 1 to 3 wherein the non-photosensitive compound is a dissolution inhibitor that has a polar group that is a keto group, the compound having an inhibition factor of at least 0.5.
- 25 5. The composition as claimed in claim 5 wherein the polar group is a vinylogous ester group, and the compound has an inhibition factor of at least 5.
- 30 6. The composition as claimed in either claim 4 or 5 wherein the compound is a xanthone, flavanone, flavone, pyrone, 2,3-diphenyl-1-indenone, or 1'-(2'-acetonaphthonyl)benzoate, and the weight ratio

of the dissolution inhibitor compound to the phenolic resin is at least 1:100.

7. A lithographic printing plate comprising
5 a support having thereon a laser-imageable, positive-working imaging layer formed from the imaging composition as claimed in any of claimed 1 to 6.

8. The printing plate as claimed in claim 7
10 wherein the support is a grained and anodized aluminum support, or a polyester support.

9. The printing plate as claimed in either
claim 7 or 8 wherein the laser-imageable positive-
15 working imaging layer is the sole radiation-sensitive layer.

10. A method for providing a positive image
consisting essentially of the steps of:
20 A) imagewise exposing the positive-working lithographic printing plate as claimed in any of Claims 7 to 9 with an infrared radiation emitting laser, and
B) contacting the element with an aqueous
developing solution to remove the imaged areas of the
25 positive-working printing plate.

INTERNATIONAL SEARCH REPORT

Int'l Patent Application No

PCT/US 98/04411

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41C1/10 B41M5/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B41C B41M G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 97 39894 A (HOARE RICHARD DAVID ; HORSELL GRAPHIC IND LTD (GB); PARSONS GARETH) 30 October 1997 see page 9, line 13 - line 17; claims 1, 16, 22	1-10
P, X	EP 0 823 327 A (MITSUBISHI CHEM CORP) 11 February 1998 see page 22, line 23 - line 26 see column 22, line 55 - column 23, line 21	1
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 150 (P-1025), 22 March 1990 & JP 02 010355 A (MATSUSHITA ELECTRIC IND CO LTD), 16 January 1990, see abstract	1
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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Date of the actual completion of the international search

16 June 1998

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 203 (P-591), 2 July 1987 & JP 62 024241 A (MITSUBISHI CHEM IND LTD), 2 February 1987, see abstract	1
A	US 5 491 046 A (DEBOER CHARLES D ET AL) 13 February 1996 see column 9, line 13 - line 44	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/04411

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		ES 2114521 T	01-06-1998
		GB 2317457 A	25-03-1998
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		EP 0845115 A	03-06-1998
EP 0823327 A	11-02-1998	NONE	
US 5491046 A	13-02-1996	NONE	

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